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Optical properties of $TiBe_2$ in the range from 0.5 to 3.3 eV

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The optical properties of polycrystalline $TiBe_2$ have been determined by ellipsometry in the visible and infrared region. The most predominant features of the spectra are in excellent agreement with a calculation of the optical conductivity.

I. INTRODUCTION

Recently there has been considerable interest in the cubic laves-phase material $TiBe_2$, primarily with a view toward its magnetic properties.[1-4] A variety of models were proposed to explain the interesting properties of $TiBe_2$: exchange enhanced paramagnetism, spin-density-wave antiferromagnetism, and metamagnetism. This confusing situation apparently asked for a more rigorous approach from fundamental origin. A first step in understanding the electronic structure was made by de Groot, Koelling, and Mueller[5] and Jarlborg and Freeman[6] who produced a relativistic augmented-plane-wave (APW) calculation for $TiBe_2$ (and $ZrZn_2$), in which the density of states and the Fermi surfaces were calculated. The equivalent spin-polarized quantities were calculated about one year later by Jarlborg, Freeman, and Koelling.[7] This stimulated experimentalists to verify the theoretical predictions. van Deursen, de Vroomen, and Smith[8] performed the first de Haas–van Alphen observation on $TiBe_2$. The same author published more extensive data.[9]

Optical measurements can provide an additional experimental test for additional energies away from the Fermi energy. Ellipsometry allows a direct determination of the dielectric properties of a material. Since it probes a much larger part of the solid compared with photoemission, surface contamination forms a less serious problem. We have interpreted the measurements on the basis of a band model and found excellent agreement between theory and experiment.

II. EXPERIMENTAL PROCEDURE

The measurements were performed in an ellipsometer, the basic details of which can be found in the work of Castelijns.[10] The instrument is semiautomatic and is based on the rotating analyzer method. During measurement the sample is kept in a vacuum chamber equipped with a magneto-ion pump permitting an ultimate vacuum of 2×10^{-9} Torr. A modification was made in so far that a small 48-kbyte (1 kbyte $=10^3$ bytes $=1024\times8$ binary digits) Rockwell International AIM-65 microcomputer was connected to the system for on-line data processing. This opened the possibility to make use of a new single wavelength *in situ* alignment procedure developed by Wijers.[11] The balancing technique also described in the same place, was used for every separate point during the measurements. As a consequence data of good reliability and repeatibility were obtained. The bulk specimen of $TiBe_2$ was prepared by means of arc melting of its constituents. The composition was stoichiometric within a 0.1% margin, as deduced from the difference in weight before and after melting. No other phases have been observed within a 5% accuracy, when the sample was observed by means of a Debye-Scherrer analysis. Laue diffraction revealed the structural nature of the polycrystalline samples as a conglomerate of several small crystallites with different orientation.

In order to obtain an optically flat surface the crystals were scoured and polished in subsequent steps, the last one being a 5-μm diamond paste. By visual inspection the surface showed a clean, metallic, silvery appearance. The sample was kept under a protective gas atmosphere before definite storage in the vacuum chamber. After opening, mounting of the sample, and closing of the system a rapid pumpdown was achieved by means of a small Balzers TPU-100 turbomolecular pump. The overall pressure in the vacuum chamber during the experiment was about 2×10^{-9} Torr. The calculation of the joint density of states for the direct transitions was based on the same APW band structure calculation as described before.[4] The 89 *ab initio* points were fitted to a symmetry-adapted Fourier series of 44 terms. The overall fitting error was about 0.01 eV. The integration over the Brillioun zone was performed as follows. A rectangulaar parallelopiped part of the Brillioun zone with corners

$$x,y,z;\quad x=0,\pi/a,\quad y=0,0.5\pi/a,\quad z=0,0.5\pi/a$$

was divided up into 2000 cubes. The reducible character of this part of the Brillouin zone was taken into account by assigning appropriate weight factors to the cubes. In each of the cubes the integration of the bands at these points were obtained by a Langrange fit to the eigenvalues of the corners of the cubes. These eigenvalues in their turn were obtained from the Fourier fit. Thus a total of 1 600 000 pseudorandom points were used in the integration.

Figure 1 shows the measured and calculated optical conductivity as a function of excitation energy. The features in the theoretical curves are labeled alphabetically.

Figure 2 shows the band structures with same labels as in Fig. 1. This interpretation of the features in the spectra was found by analysis of the calculation of the joint density of states. The arrows mark van Hove singularities. The first peak structure called A mainly arises from transitions be-

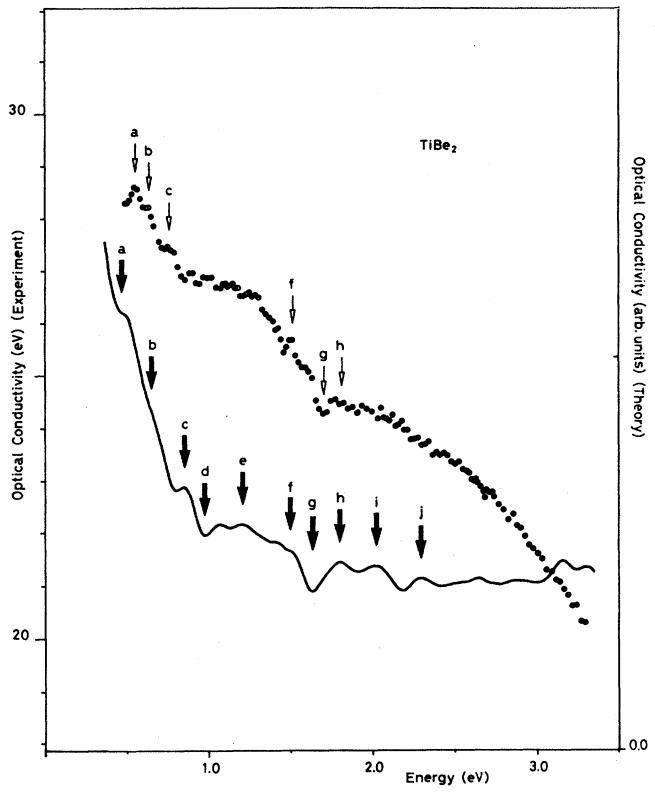

FIG. 1. Calculated joint density of states (solid line) and experimental optical conductivity (circles) for $TiBe_2$.

tween bands 7 to 9 around the D line. There is some contribution from excitations from 8 and 9 to band 10 along Δ. This minor contribution is not indicated in Fig. 2. Feature B is clearly connected with excitations from 8 and 9 to 10 around Σ. Peak C shows the biggest disagreement between theory and experiment (0.84 eV vs 0.76 eV).

In the theoretical model the transition is located very close to L. Selection rules forbid the transition at L however. This selection rule is relaxed once one moves outside L. Along the Λ line the exitation energy increases. However, very soon the empty final-state bands 8 and 9 get occupied. Along the Q and G line, however, the excitation energy decreases. Thus we expect the peak C as calculated to shift to lower energies once matrix elements are included. This model is supported by the calculation of the position in the zone where transition occurs at the experimental excitation energy (0.76 eV). This is exactly what the direct model gives, but it would be more closely towards U and W.

Feature E is not resolved in the spectrum. Peak F finds its origin in transitions from bands 5–9 and 6–10 just outside W. Transition has a similar origin as peak b; excitations take place here from band 5, however. Peaks I and J are not found back in the experimental spectrum with significant signal-to-noise ratios.

Let us compare the found transitions with the electronic structure of isoelectronic and isostructural $ZrZn_2$. A crucial difference between $TiBe_2$ and $ZrZn_2$ as well as between $TiBe_2$ and $TiBe_{2-x}Cu_x (x \geq 0.15)$ is the position of the van Hove singularity in bands 7 and 8 near W.[4] In $TiBe_2$ this van Hove singularity is below E_F leading to a Fermi surface with closed X centered hole sheets, while in $ZrZn_2$ and

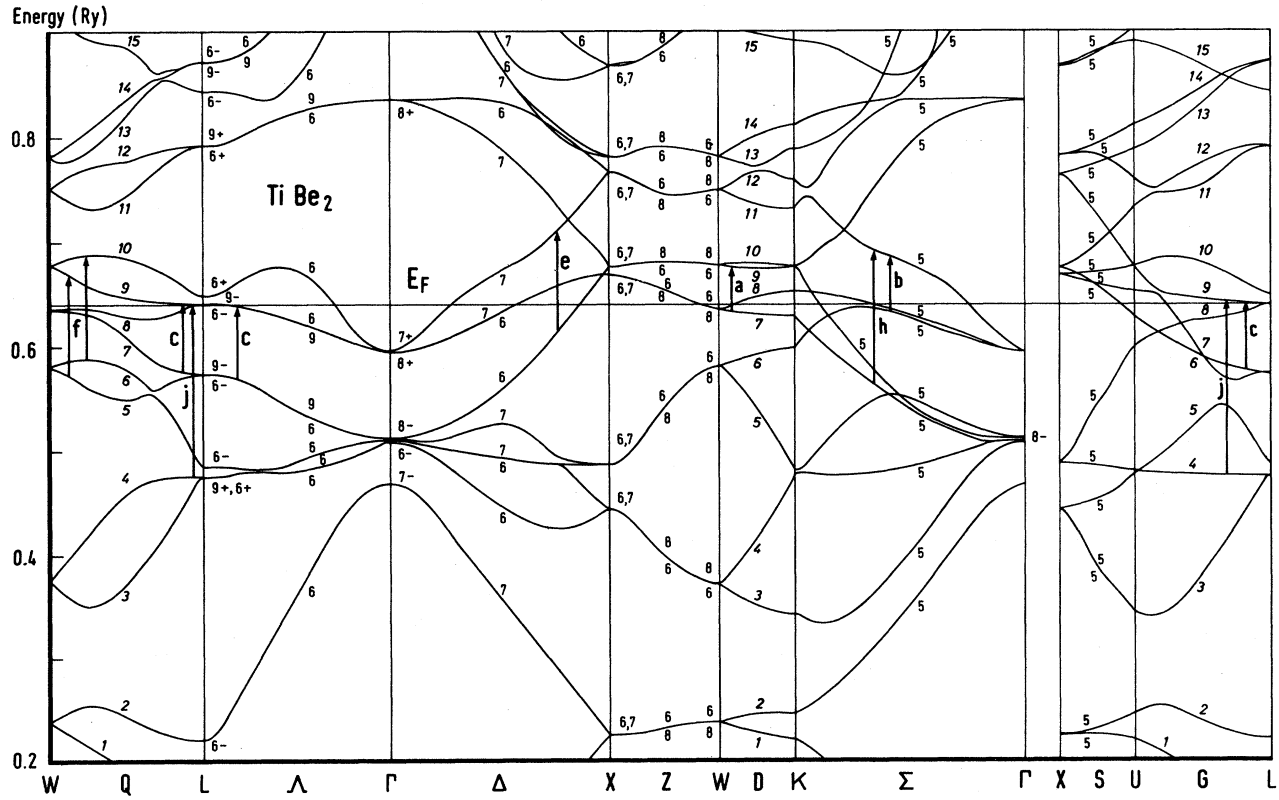

FIG. 2. The band structure of $TiBe_2$. Arrows and letters refer to features in the optical conductivity of Fig. 1. Numbers are symmetry labels of the (relativistic) irreducible representations, italic numbers are band numbers.

$TiBe_{2-x}Cu_x$ these singularities lie above E_F leading to open cagelike structures, connecting the X points (so-called "jungle gyms"). The fact that there is a clear transition (a) from band 7 (below E_F) to band 9 strongly supports these models; at least for $TiBe_2$. We predict that the transition will vanish on substituting Be for Cu in $TiBe_{2-x}Cu_x$ and will also be absent in $ZrZn_2$.

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